

# Network formation and relaxation dynamics in a new model for colloidal gelation.

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## Abstract

We investigate the gel formation from the equilibrium sol phase in a simple model that has the characteristics of (colloidal) gel-forming systems at a finite temperature. At low volume fraction and low temperatures, particles are linked by long-living bonds and form an open percolating network. By means of molecular dynamics simulations, we study the lifetime of bonds and nodes of the gel network in order to relate these quantities to the complex relaxation dynamics observed.

*Key words:* Gels, network formation, glassy dynamics.

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## 1 Introduction

Gels are a special case of slow and disordered systems: Due to the low volume fraction, their slow dynamics are intimately related to the formation of an open structure (1). The understanding of the connection between the structure of these systems and their complex dynamics is fundamental in the research on complex fluids, such as biological systems, polymeric materials, and colloids. The slow dynamics of gelling systems have some analogies with the dynamics of other disordered systems such as dense glasses, in that the majority of the particles becomes temporarily localized in space due to the structure formation. On the other hand, due to the presence of the network, the gels show relaxation dynamics which strongly depend on the length scale/wave vector considered. At small wave vectors and close to the gelation threshold one typically observes very slow stretched-exponential and power law relaxations. Surprisingly, at higher wave vectors, recent experimental work on colloidal gels shows the onset of a compressed exponential relaxation (i.e. Kohlraush

exponent  $\beta > 1$ ) (2). This non-trivial behavior is the subject of an intense debate in the last years. In particular, it is still not clear how is it related to the structural features of the gel.

Numerical simulation studies offer an effective tool in that they allow to follow the local relaxation processes and to understand their role in the complex dynamics. In spite of this, progress has also been hampered by the fact that there are so far very few microscopic realistic models for gels that effectively allow to study their dynamics by means of analytical methods or computer simulations. In colloidal systems the interparticle interactions can be suitably tuned: First, particles can be coated and stabilized leading to a hard sphere behavior. Then, an attractive depletion interaction can be induced by adding some non-adsorbing polymers. The range and strength of the potential are controlled by the size and concentration of the polymer respectively (3). For volume fractions from 3% up to 40% and attractive interaction energies of the order of  $k_B T$  confocal microscope images (4) show the formation of persistent structures, different at different volume fractions, and gel phases, whose mechanisms of formation are still poorly understood. It is important to note that here the underlying thermodynamics may significantly interplay and/or compete with gel formation via phase separation or microphase separation. As a consequence, coarsening or ordering processes will interfere with the gel dynamics. Whereas in the experiments the time scales typical of the micro or macro-phase separation are often much longer than the observation time scales, this is not the case in numerical studies using traditional models for colloidal suspensions, where the investigation of the gel dynamics has been severely hindered until very recently.

In order to overcome these difficulties, we have recently proposed a new model (5; 6) consisting of meso-particles which interact via a short range attraction of the type already used to study colloidal systems. We have started from the idea that, in order to obtain a persistent open structure, a mechanism competing with phase separation processes is needed. The novelty of our model is to include a directional effect in the interactions and therefore to facilitate the formation of the open structures found in gelling systems. These directional interactions are given by a combination of site-site interactions of the particles as well as a short ranged three-body interaction. Thus this new approach will promote the formation of large-scale disordered structures that are stable also at relatively high temperatures, without imposing a fixed local functionality of the meso-particle. It should also be noted that the presence of directional effective interactions, although not yet thoroughly investigated, is likely to play an important role in the physics of colloidal gels. This is supported by the experimental observation of the local rigidity of the structures and of their low local connectivity: The open structures which spontaneously form at low volume fractions are characterized by aggregating units (particles or aggregates of particles) with a coordination number between 3 and 4 (7). In addition, surface inhomogeneities or sintering of the particles which are present in many cases can produce quite rigid links (8).

In this paper, we analyze the formation of the gel network in this model and focus on the time autocorrelation of bonds and network nodes. This study is essential to make the connection between the features of the network structure and the onset of the complex dynamics of the gel phase (6).

In the following we briefly present the model and the numerical study in Sec. 2. We then describe the aggregation process and the structure of the gel phase in Sec. 3. In Sec. 4 we study the time autocorrelation functions and the lifetime of bonds and of the nodes of the network structure. Finally, conclusions drawn from the results of the numerical study are contained in Sec. 5.

## 2 Model and numerical simulations

The model investigated consists of identical particles of radius  $\sigma$ , interacting via an effective potential  $V_{\text{eff}}$  that is the sum of a two- and three body terms. The two body potential is itself the sum of a hard core like interaction that is given by a generalized Lennard-Jones potential,  $V_{\text{LJ}}(r)$ , and a term  $V_{\text{cp}}$  that depends on the relative orientation of the particles. For the radial term we have used  $V_{\text{LJ}}(r) = 23\epsilon[(\sigma/r)^{18} - (\sigma/r)^{16}]$  where the prefactors and exponents have been chosen in such a way to give a relatively narrow well of depth  $\epsilon$ . In the following we will measure length and energy such that  $\sigma = 0.922$  and  $\epsilon = 1$ , respectively, and time in units of  $\sqrt{m\sigma^2/\epsilon}$ , where  $m$  is the mass of a particle.

As already discussed in the previous section, we have introduced a mechanism that favors the formation of an open network structure, in competition with the phase separation induced by purely radial interactions. This has allowed us to obtain an open persistent structure at temperatures and volume fractions where phase separation or microphase separation do not occur and therefore to study the dynamics of the gel formation without the complex interplay with the underlying thermodynamics. In practice, we have introduced a directional interaction by decorating each particle with 12 points that form a rigid icosahedron inscribed in a sphere of diameter  $1.1\sigma$ . The potential  $V_{\text{cp}}$  between a particle #1 with a particle #2 is then set up in such a way that it is more favorable that the center of particle #1 approaches particle #2 in the direction of one of the points of the icosahedron that decorate particle #2. In addition we have also included an explicit (short range) three body potential  $V_3$  in the form of a gaussian in the angle  $\theta$  between three neighboring particles and which makes that values of  $\theta$  smaller than  $0.4\pi$  are unlikely. Although recently 3-body interactions have been directly measured amongst charged colloidal particles (9), one could more generally see the particles in our model as the building blocks of the gel network (i.e. particles or aggregates of particles). In this terms, our model is aimed to describe the presence of directional effective interactions at some mesoscopic length scale, leading

to the formation of the open structures. More details on these potentials will be given elsewhere (10), but here it should be noted that, whereas  $V_3$  is a real 3-body term introducing an angular rigidity,  $V_{cp}$  is a geometric term which allows to add a soft-sphere repulsion depending on relative orientation. This term is not able alone to effectively limit the functionality of the particles at the volume fraction and temperatures considered here. The choice of considering the effect of both these terms has been made in the spirit of investigating more deeply their relative contribution to the formation of the open network (and to its dynamics). For example, by taking only  $V_{LJ} + V_3$  an open structure can certainly be obtained, but probably slightly different from the one discussed here. For the moment a complete understanding of the interplay of these two terms has not been reached yet.

On the whole, in our model the (meso) particles can form directional bonds that favor the formation of an open network structure, without, however, imposing a local symmetry or connectivity, in contrast to models that have been proposed before (11; 12). As a consequence, in our case there is an *effective* functionality of the particles, which is the result of the competition between entropic and internal energy contribution in the network formation.

Using these interactions, we have done microcanonical simulations using constrained molecular dynamics and a suitable combination of the algorithms RATTLE and SHAKE (13) with a step size of 0.002. The number of particles was 8000 and the size of the simulation box  $L = 43.09$  which gives a volume fraction of 0.05. (This corresponds to a particle density of 0.1) Before starting the production runs we carefully equilibrated the system by monitoring that the relevant time correlation functions have attained their asymptotic limit. The temperatures investigated were 5.0, 2.0, 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, and 0.05. In order to improve the statistics of the results we have averaged them over five independent runs.

### 3 Structure and cluster formation

The change of the topology of the structure with decreasing  $T$  can be characterized by investigating the coordination number  $c(n)$ , which is shown in Fig. 1 as a function of the inverse temperature. We define  $c(n)$  as the fraction of particles that have exactly  $n$  neighbors. (Two particles are considered to be neighbors if their distance is less than  $r_{\min}=1.1$ , the location of the first minimum in the radial distribution function.) We see that at high temperatures a large majority of the particles are isolated ( $n = 0$ ). By lowering the temperature, the number of these free particles rapidly decreases and they practically disappear. The fraction of dimers or chain ends,  $n = 1$ , is around 30% at high  $T$ . With decreasing  $T$  such fraction increases, it attains a maximum at around  $T = 0.15$ , and then decreases quickly with decreasing  $T$ . At the same time the

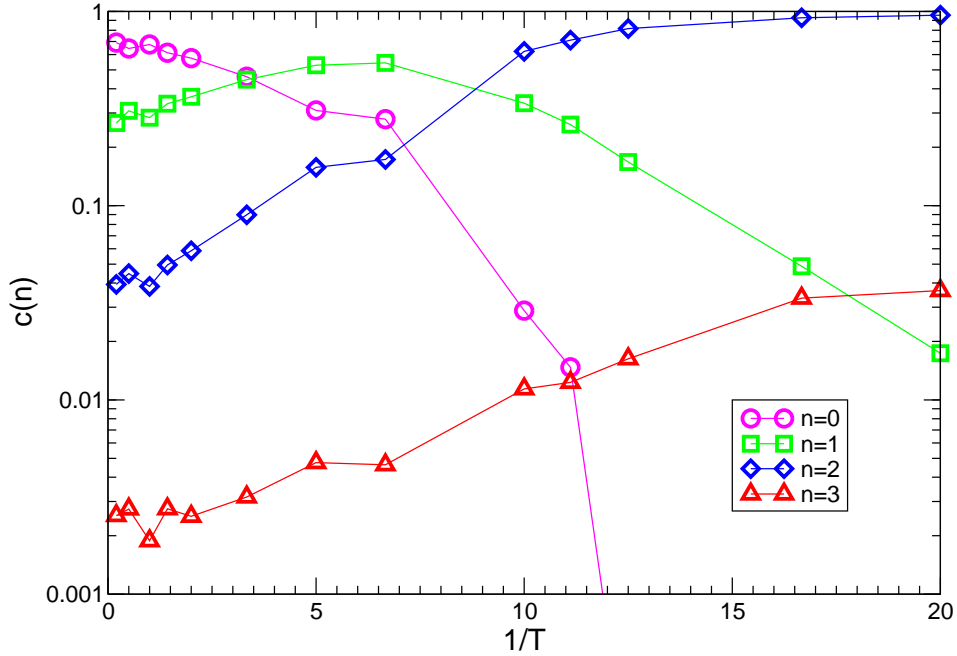


Fig. 1. (Color online)  $T$ -dependence of  $c(n)$ , the fraction of particles having coordination number  $n$ .

number of particles that have exactly two nearest neighbors increases rapidly and these (local) configurations become by far the most prevalent ones at low  $T$ . Last not least also the number of particles with  $n = 3$  neighbors increases quickly with decreasing  $T$ . From these curves we thus can conclude that with decreasing  $T$  the system forms an open network in which most particles form chains that meet at points with coordination number three and which are thus important for the mechanical properties of the structure. We have also shown elsewhere (5; 6) that whereas at high  $T$  the static structure factor  $S(q)$  of the system is relatively flat, i.e. the system has a structure similar to the one of a gas of free particles, around  $T = 0.1$   $S(q)$  starts to show a peak at  $q_0 = 7.7$ , a wave-vector which corresponds to the distance between two nearest neighbor particles. In addition  $S(q)$  shows an increase at small  $q$  which indicates the formation of a disordered open network structure. This increase is relatively moderate and does not strongly depend on  $T$ , giving evidence that the system does not undergo a phase separation even at the lowest temperatures considered. Moreover,  $S(q)$  does not show any pronounced peak at these low wave-vectors and thus we can conclude that the network is disordered and does not have a well defined length scale.

The appearance of the peak at  $q_0 = 7.7$  is due to the fact that at intermediate and low  $T$  the particles condense into clusters. By defining that a particle belongs to a cluster if its distance from at least one member of the cluster is less than  $r_{\min}$ , we have studied  $n(s)$ , the number of clusters that have exactly  $s$  particles (5). For  $T \geq 0.3$  this distribution follows an exponential law,

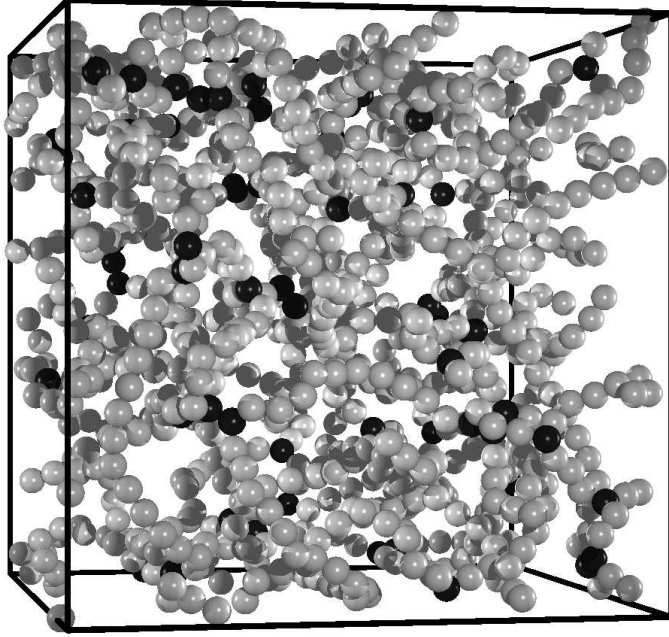


Fig. 2. Part of a configuration, a cube with side  $L/2$ , of the system at  $T = 0.05$ . The light and dark particles have coordination  $n = 2$  and  $n = 3$ , respectively.

corresponding to the random formation of transient clusters of non-bonded particles at low densities. Coherently with the data shown in Fig.1, at  $T = 0.1$  the shape of the distribution has strongly changed in that now the most probable clusters have size  $s = 2$ . At the same time  $n(s)$  has grown a tail at large  $s$  in that the largest clusters found have now  $O(100)$  particles. At lower temperatures,  $n(s)$  crosses over to a power law regime for high values of  $s$ , with a crossover point that moves to larger  $s$  with decreasing  $T$ . At  $T=0.06$  this regime is apparently compatible with random percolation (14). At the lowest temperatures,  $T \leq 0.06$ , the distribution shows a gap at large  $s$  in that the system can form one big cluster that contains a substantial fraction of the particles in the system. Finally at  $T = 0.05$  we have only very few particles that are members of small clusters, with an  $n(s)$  that is basically a constant, whereas the overwhelming majority ( $> 97\%$ ) of the particles belongs to one large percolating cluster. Hence, at very low temperatures it is energetically very unfavorable to have free particles and small free clusters.

In Fig. 2 a typical configuration at  $T = 0.05$  is shown: An open network in which most particles are forming chains (light spheres) that are connected in a relatively random way at points that have three or more neighbors (dark spheres).

## 4 Dynamics: Lifetimes of bonds and nodes of the network

Having characterized the structure of the system, we now turn our attention to its dynamical properties. We have studied the mean-squared displacement of a tagged particle,  $\langle r^2(t) \rangle = \langle |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle$ . A detailed discussion of the time dependence of  $\langle r^2(t) \rangle$  can be found in Ref.(6). Using this function and the Einstein relation we obtained the diffusion constant  $D(T)$ . Furthermore we have calculated the self-intermediate scattering function  $F_s(q, t)$  for wave-vector  $q$ ,  $F_s(q, t) = N^{-1} \sum_{j=1}^N \langle \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \rangle$ . The discussion of the quite complex  $q$  and  $T$  dependence of  $\langle r^2(t) \rangle$  and  $F_s(q, t)$ , characteristic for a gel-forming system, has also been presented elsewhere (6). From these functions we have calculated the characteristic relaxation times  $\tau_s(q, T) = \int F_s(q, t) dt$ .

Here we focus on the time autocorrelation functions of bonds and nodes forming the gel network. This analysis is essential to understand the role of different parts of the structure in the complex dynamics observed. As in Fig.2 we make the distinction of bonds that are connected to particles that have a coordination number of three (referred to as “anchor particles”) from the bonds that are connected to particles that have a coordination number of two (“bridging particles”). For this we have determined  $C_b(t)$ , the probability that a bond that exists at time zero is still present at time  $t$ , defined as

$$C_b(t) = \frac{\sum_{ij} [\langle n_{ij}(t) n_{ij}(0) \rangle - \langle n_{ij} \rangle^2]}{\sum_{ij} [\langle n_{ij}^2 \rangle - \langle n_{ij} \rangle^2]}, \quad (1)$$

where  $n_{ij}(t) = 1$  if particles  $i$  and  $j$  are linked at time  $t$  and  $n_{ij}(t) = 0$  otherwise. We have also calculated the corresponding time correlation function for the anchor points  $C_{3b}(t)$  defined as

$$C_{3b}(t) = \frac{\sum_i [\langle n_{3i}(t) n_{3i}(0) \rangle - \langle n_{3i} \rangle^2]}{\sum_i [\langle n_{3i}^2 \rangle - \langle n_{3i} \rangle^2]}, \quad (2)$$

where  $n_{3i}(t) = 1$  if particles  $i$  is an anchor point at time  $t$ ,  $n_{3i}(t) = 0$  otherwise. We have determined the corresponding average lifetime of bonds and anchor points as  $\tau_b(T) = \int C_b(t) dt$  and  $\tau_{3b}(T) = \int C_{3b}(t) dt$ , respectively. In Fig. 3 these quantities are plotted in an Arrhenius plot together with the relaxation times  $\tau_s(q, T)$  obtained from the incoherent scattering functions  $F_s(q, t)$  for different wave-vectors  $q$  and the inverse of the diffusion constant  $D(T)$  (5). This figure well elucidates the role of bonds and nodes in the fundamental difference between the high  $T$  and the low  $T$  regime of the relaxation dynamics: At low temperatures (i.e.  $T \leq 0.1$ ) the bond lifetime sets the longest relaxation time scale in the system, and it becomes much longer than the simulation time window at the lowest  $T$ . That is, whereas at high temperatures the relaxation in the system is dominated by particle collision and diffusion, at the temper-

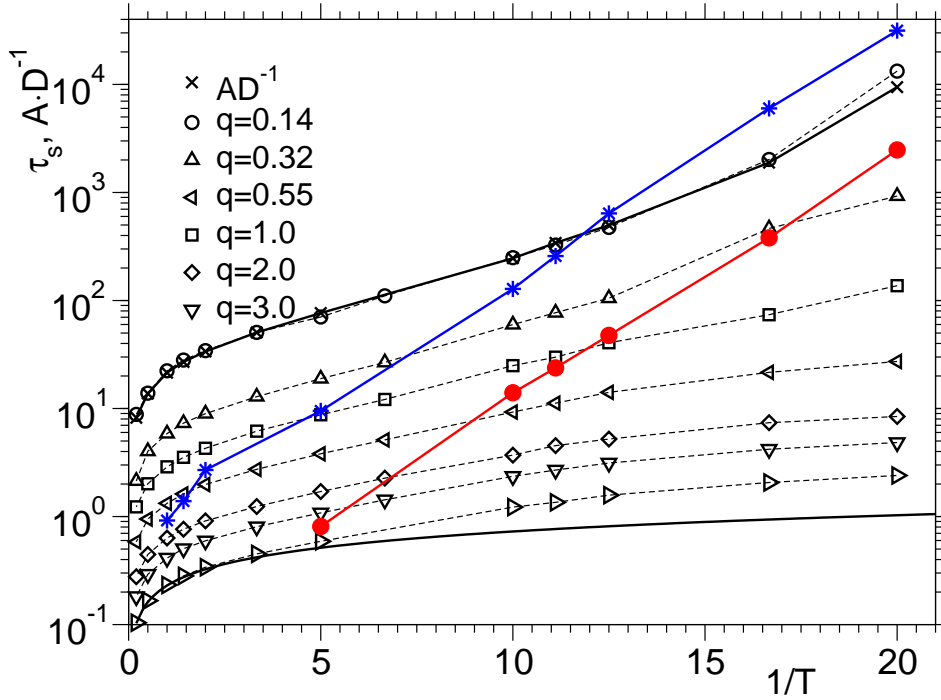


Fig. 3. (Color online) Arrhenius plot of the diffusion constant  $D$  and of the relaxation time  $\tau_s(q, T)$  as determined from the self-intermediate scattering function  $F_s(q, t)$ . The solid line is a fit to the high  $T$  data for  $q = 3.0$  of the form  $\tau = \text{const.}/\sqrt{T}$ . The open symbols correspond to different wave-vectors. The stars and filled circles are  $\tau_b$  and  $\tau_{3b}$ , respectively.

atures where the aggregation starts to produce persistent structures the main mechanism for the relaxation is the bond breaking.

From the figure, we recognize that at high  $T$  the relaxation time  $\tau_s(q, T)$  follows a  $T^{-0.5}$ -dependence for all  $q$ , which can easily be understood from the ballistic motion of the free particles and the small clusters. (Recall that in this  $T$ -range the distribution of the cluster size is independent of  $T$  (5).) For wave-vectors that are large,  $q \geq 2.0$ , the  $T$ -dependence of  $\tau_s(q, T)$  at low temperatures is relatively weak but still somewhat stronger than  $T^{-0.5}$ . This can be understood by realizing that on the corresponding length scales the particles can still undergo an (almost) ballistic motion, despite the fact that they are, at low  $T$ , connected to other particles, since the whole local structure is moving ballistically. This type of motion is no longer possible if one considers length scales that become comparable to the size of the mesh of the network which is around 10 and thus corresponds to a  $q$  smaller than 1.0. For  $q = 0.55$  we find at low temperatures a  $T$ -dependence of  $\tau_s$  that is close to an Arrhenius law whereas for smaller wave-vectors we find an even stronger  $T$ -dependence. On length scales that are thus comparable or larger than the typical mesh size of the network the  $T$ -dependence is thus very similar to the one characterizing the slow dynamics of dense glasses.



Also included in Fig. 3 is the inverse of the diffusion constant  $D$ , scaled by a factor  $A = 49.2$  in order to make it coincide with the value of  $\tau_s(q = 0.14, T = 1.0)$ . We find that in the whole  $T$ -range investigated this quantity follows very closely the  $T$ -dependence of  $\tau_s(q, T)$  for small  $q$ , which is evidence that in this system the relaxation of the structure is closely linked to the diffusive motion of the particles, in contrast to the behavior found in dense glass-forming systems in which dynamical heterogeneities make that the  $T$ -dependence of  $D$  is weaker than the one of  $\tau_s$  (15). This behavior corresponds to the lowest temperature dynamical regime associated to the presence of the persistent network.

Since here we would like to point out in particular the features of bond and nodes correlation at low  $T$ , we note that for  $T \leq 0.1$ ,  $\tau_b$  shows an Arrhenius dependence on the temperature, in agreement with the picture mentioned above. As shown in the figure, the lifetime of the bonds is around a factor of 20 larger than the one of the anchor points, but the  $T$ -dependence is the same. This result is reasonable since the anchor particles experience on average more mechanical stress than the bridging particles and, due to their higher coordination, have less possibilities to yield to this stress. Hence it is more likely that their bonds are broken. Fig.3 also shows that the low  $T$  regime associated to the presence of the network, whose complex dynamics have been studied in Ref.(6), corresponds to  $\tau_b$  being the longest time scale and  $\tau_{3b}$  becoming of the order of the longest relaxation times in the system. At these temperatures, there are practically no free particles (see Figs.1 and 2) and more than 97% of them belong to the spanning network. Therefore one can envision the relaxation process in this system that the connecting branches of the network detach from the anchor particles, the branch reorients and attaches itself to a different branch, thus creating a new anchor point. Of course, the possibility that a branch breaks at a bridging particle can not be neglected completely since there are significantly more bridging particles than anchor particles. Thus this type of motion will contribute to the relaxation dynamics as well.

Let us now see how the time dependence of bond and nodes correlations at different temperature can be connected to the scenario just presented. In the main panel of Fig. 4,  $C_b(t)$  is plotted as a function of the time for different temperatures  $T$ . Although the long time decay of these functions is well described by a single exponential law at all the temperatures, we can actually distinguish two different regimes, one of high temperatures ( $T > 0.1$ ) and the low temperature regime, corresponding to  $T \leq 0.1$ . At high temperature the particle collisions promote uncorrelated bond breaking or formation leading to a short time decay of bond correlation whose amount monotonically decreases with temperature. At long times the bond breaking due to the energy activation process will eventually lead to the complete decay of correlations. At low temperatures instead, the energy activation process appears to be the only relevant process in the decay of bond correlation (due to the less and less important role of particle collisions).

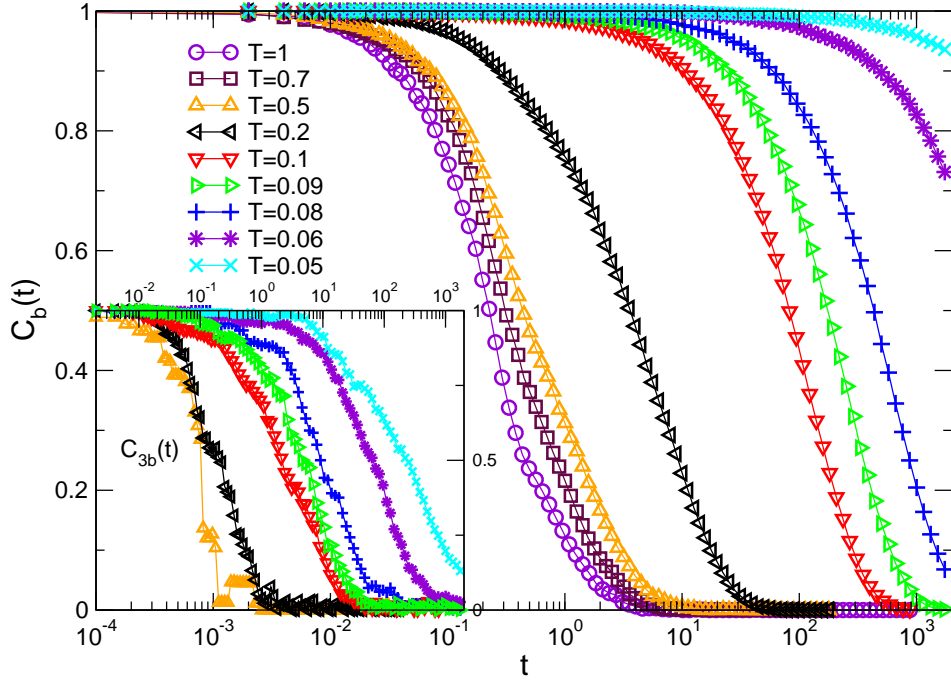


Fig. 4. (Color online) **Main panel:** Bond correlation function  $C_b(t)$  for different temperatures  $T$ . **Inset:** Time correlation function of the anchor points of the network,  $C_{3b}(t)$ , for different temperatures  $T$ .

In the inset of Fig. 4,  $C_{3b}(t)$  is plotted as a function of the time for different temperatures. At the higher temperatures ( $T > 0.1$ ) at this volume fraction particles of connectivity 3 are extremely rare, as already shown by Fig. 1. As long as a spanning network is not formed, i.e. at temperatures  $T \geq 0.06$ , the long time decay of time correlation functions  $C_{3b}(t)$  follows a simple exponential law, whose characteristic relaxation time increases with decreasing  $T$ . In addition to this regime, at temperatures when a persistent spanning network is present in the system, i.e.  $T \leq 0.055$ , the decay of  $C_{3b}(t)$  becomes also stretched, with a stretching exponent  $\beta$  decreasing with  $T$  ( $\beta \simeq 0.55$  at  $T = 0.05$ ). This indicates that, once the network is formed and it is sufficiently persistent, the breaking and formation of the nodes will be associated not only to the overcoming of an activation energy but also to some heterogeneous and cooperative dynamic process (6; 10).

The scenario emerging from these data can be interestingly connected to the detailed analysis of the wave vector dependence of  $\tau_s(q, T)$  presented in Ref.(6). There we have discussed the striking differences between the high temperature and low temperature regime of the time correlations of particle displacement. At high temperatures, by decreasing the wave vector,  $\tau_s(q, T)$  smoothly crosses over from a ballistic to a diffusive type of behavior with an exponential decay of time correlations. At low temperatures, instead, once that a permanent spanning network is present, two clearly different regime, respectively at high

and low wave vectors, can be individuated. We have been able to show that the relaxation at high wave vectors is due to the fast cooperative motion of pieces of the gel structure, whereas at low wave vectors the overall rearrangements of the heterogeneous gel make the system relax via a stretched exponential decay of the time correlators. The coexistence of such diverse relaxation mechanisms is apparently determined by the formation of the gel network (i.e. the onset of the elastic response of the system) and it is characterized by a typical crossover length which is of the order of the network mesh size.

## 5 Conclusion

We have analyzed the structural and dynamical features in the gel formation by molecular dynamics simulations of a new model for colloidal gels, based on directional effective interactions. We have focused on the change in the topology corresponding to the formation of the gel network and on the time correlation of bonds and nodes of the gel network. Our analysis shows that, once that bonds are practically permanent over the simulation time window, the onset of the persistent network corresponds to the onset of some heterogeneous and complex dynamics, which is directly related to the anchor points of the network. It is evident that the anchor points are very important for the mechanical stability of the structure. On length scales of the order of the interparticle distance the structure is quite flexible whereas on the scale of the mesh size of the network, which is given by the typical distance between the anchor points, the structure becomes somewhat more rigid due to the constraints imposed by the enhanced connectivity. However, even on that length scale the system is relatively soft as compared to the one found in dense glasses. With decreasing temperature the connecting chains will become stiffer and hence give rise to an increased effective interaction between the anchor points (6; 10).

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